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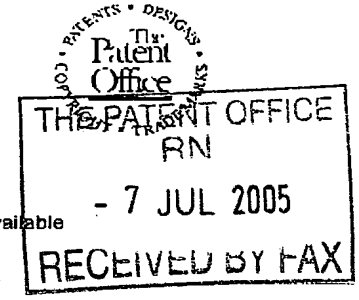

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Request for grant of a patent

(An explanatory leaflet on how to fill in this form is available from the Patent Office)

0513985.2

- 7 JUL 2005

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1 Your reference: *(optional)* MDX,031-P-UK

J116417/ 001 D01049 P01/77H0FEE....
11JUL05 0-00 NONE 0513985.2

2 Full name, address and postcode of the applicant or of each applicant *(underline all surnames)*:

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Patents ADP number *(if you know it)*: 8940447002

If the applicant is a corporate body, give the country/state of its incorporation: English

3 Title of the invention: SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE

4 Name of your agent *(if you have one)*:

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"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Patents ADP number *(if you know it)*: 05815709001

	Country	Application number *(if you know it)*	Date of filing *(day/month/year)*
5 Priority declaration: Are you claiming priority from one or more earlier-filed patent applications? If so, please give details of the application(s):			

	Number of earlier UK application	Date of filing *(day/month/year)*
6 Divisionals etc: Is this application a divisional application, or being made following resolution of an entitlement dispute about an earlier application? If so, please give the application number and filing date of the earlier application:		

7 Inventorship: (Inventors must be individuals not companies) (Please tick the appropriate boxes)

Are all the applicants named above also inventors? YES [ ] NO [x]

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9 Accompanying documents: not counting duplicates, please enter the number of pages of each item accompanying this form:

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Description: 5

Claim(s): 2

Abstract: 1

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If you are not filing a description, please give details of the previous application you are going to rely upon:

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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*: 1 + 1

Request for search *(Patents Form 9A/77)*:

Request for substantive examination *(Patents Form 10/77)*:

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11 I/We request the grant of a patent on the basis of this application.

Signature(s): Paul Cole Date: 07 July 2005

12 Name, e-mail address, telephone, fax and/or mobile number, if any, of a contact point for the applicant: Paul Cole – 0188-362-6211 e-mail pcole@lucas-uk.com

SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE

FIELD OF THE INVENTION

The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. Silver brazing alloys are also known in the silversmithing trade as silver solders or solders and these terms are used interchangeably herein.

BACKGROUND TO THE INVENTION

Various silver-based alloys of the silver-copper-zinc type are useful as solders (brazing materials). Brazing has been defined as a joining process in which a filler metal is used which has a melting point of above 450°C, but below that of the parent metal and which is distributed in the joint by capillary attraction.

Silver, copper and zinc form a ternary eutectic with a silver content of 56% and melting at 665°C, see a ternary phase diagram which is given in Fig. 2 of Jacobson et al, *Development of new silver-free brazing alloys for steel tubular assembly*, supplement to the Welding Journal (sponsored by the American welding Society/Welding Research Council), August 2002, pages 149-S to 155-S downloadable from http://www.aws.org/wj/supplement/08-2002-JACOBSON-s.pdf,. A commercially supplied silver alloy recommended by the AWS for brazing mild steel or copper has the composition of 44 wt % Ag, 30 wt % Cu and 26 wt % Zn. Such an alloy has too low silver content for use in silversmithing, where solder alloys of at least 55 wt % Ag are the norm.

Depending on their melting temperatures, brazing alloys for use in silversmithing are classified as Easy, Medium and Hard, and the major UK suppliers quote the values below:

Thessco	Solidus	Liquidus
Easy	705°C	725°C
Medium	720°C	765°C
Hard	745°C	778°C

Johnson Matthey	Solidus	Liquidus
Easy	705°C	723°C
Medium	720°C	765°C
Hard	745°C	778°C

An alloy containing 75 wt % Ag, 22 wt % Cu and 3 wt % Zn is known and provides a good colour match for silver, but is high melting. An alloy with 70 wt % Ag, 20 wt % Cu and 10 wt % Zn is also of good colour and is lower melting, and a further alloy containing 65 wt % Ag, 20 wt % Cu and 15 wt % Zn is still lower melting, see http://www.wlv.com/joining/silvabrazrefchart.xls. This is, of course, only one web page from one of the various suppliers of solder alloys for silversmiths.

A corrosion-resistant silver solder for use in the electronics industry is disclosed in JP 61078592 (Kyocera) and is based on Ag, 0.05-19 wt %, Ge, 0.01-1.0 wt % Pd, and 0.01-2 wt % Li. An exemplified composition contains Ag 94 wt %, Ge 4 wt %, Pd 0.5 wt %, Li 0.5 wt %, Fe 0.5 wt % and Ni 0.5 wt %, and another exemplified composition has Ag 80%, Ge 11.95%, Pd 8% and Li 0.05%. Recommended amounts of germanium are relatively high. For silversmithing, the use of palladium is to be avoided, as is the use of lithium even in trace amounts. Although spreadability and wettability are said to be desirable properties, colour match to the material being soldered is not necessary.

Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) discloses a novel silver alloy that maintains the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys are ternary Ag-Cu-Ge alloys containing at least

92.5 wt% Ag, 0.5-3 wt % Gc and the balance, apart from impurities, copper. Patents US-A-6168071 and EP-B-0729398 (Johns) disclose a silver/germanium alloy which comprises a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains elemental boron as a grain refiner at a concentration of greater than 0 ppm. and less than 20ppm. Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade name Argentium (Ag 92.5 wt%, Cu 6.3 wt%, Gc 1.2 wt %), and the word "Argentium" as used hercin refers to these alloys.

WO 2005/051953 (the contents of which are incorporated herein by reference) discloses a silver solder alloy of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt % Gc. The Ag-Cu-Zn alloy typically contains 55-77 wt % Ag, 10-30 wt% Cu (preferably 56-75 wt %) and 8-15 wt % Zn. The above alloys can exhibit an advantageous combination of relatively low melting point, high flowability and good colour. In particular, such alloys may have a solidus temperature in the range of about 700 to about 750°C and a liquidus temperature in the range of about 725°C to about 780°C. They can be used for soldering or brazing jewellery metals including grades of silver such as Sterling. They are particularly advantageous for soldering Argentium silver.

SUMMARY OF THE INVENTION

We have now found that solders of the "hard" category can be provided that have unusually high silver contents and correspondingly low zinc contents, and that these exhobit good colour and other properties.

The invention provides silver solders or brazing alloys of the Ag-Cu-Zn family containing more than 70wt % Ag and from 0.5 to 3 wt% Ge.

DESCRIPTION OF PREFERRED FEATURES

Preferred solders contain 1.0-2.5 wt % Ge especially about 1.5 wt % Ge and optionally may further comprise 1-3 wt % Sn, especially about 1 wt % Sn. They may contain 3 – less than 8 wt% Zn, typically 4 - 5 wt% Zn, and they may further comprise 0.05-0.4 wt % Si e.g. about 0.1 wt% Si. Too large a proportion of Si gives rise to brittleness. It may further comprise an amount of boron of e.g. 1 ppm-0.3 wt % boron, and more typically 0.1-0.3 wt % of boron which reduces grain size and helps in rolling or drawing the composition. An embodiment of the solder contains about 75 wt% Ag, about 18 wt% Cu and about 4.5 wt% Zn, about 1.5 wt% Ge and about 1 wt% Sn.

The alloys of the invention may be provided any form that is convenient for silversmithing, e.g. rod, strip, wire, fine particles or a paste in which powdered metal is suspended in a vehicle, and may be used with conventional fluxes. In the case of pastes, US-A-5443658 (Hermanek) discloses a vehicle which is an aqueous gel containing 78 weight percent water, 10 weight percent mineral oil, 10 weight percent glycerin with the balance sodium carboxymethyl-cellulose. US-A-5120374 (Mizuhara) discloses gels containing 1-4 wt. % hydroxypropylcellulose, 40-80 wt. % 1,2-propanediol, 18-58 wt. % 2-propanol or 1-4 wt. % hydroxypropylcellulose, 20-70 wt. % 1,2-propanediol, 26-76 wt. % water. US-A-4475959 discloses an organic vehicle system based on resins dispersed in hydroxylic solvents. Low-melting hydrocarbon vehicles may also be used. Useful materials include those melting below room temperature to normally solid materials, e.g. C_{18}-C_{60} petroleum hydrocarbon waxes melting from 28°C. to 100°C. Such materials should have a low ash or solid residue content and either melt and flow, sublime and/or thermally decompose below 500°C. Useful hydrocarbons may be paraffinic, aromatic, or mixed aromatic paraffinic or mixtures of compounds of such characteristics, and include various mixtures of hydrocarbons, e.g., octadecane, mineral spirits, paraffin wax, and petrolatum (a colloidal system of non-straight-chain solid paraffinic hydrocarbons and high boiling liquid paraffinic hydrocarbons, in which most of the liquid hydrocarbons are held inside the micelles), e.g., Vaseline.

The alloys can be used in any conventional soldering or brazing method e.g. using a hand torch, a fixed burner, induction or resistance heating or using a brazing furnace, preferably such a furnace which provides a protective atmosphere.

The invention is further illustrated in the following examples

Example 1

A brazing composition is prepared by melting together the following materials:

Ag	-	75%
Ge	-	1.5%
Sn	-	1.0%
Zn	-	4.5%
Cu	-	18%.

The resulting composition is expected to roll well from cast ingot (satisfactory to 40% work hardened, then required annealing) and is a good solder when tested initially on gilding metal samples. The solder composition runs well along a 'T' join. The observed colour is good. On tarnish testing the present solder appears bright. Its melting point is within the range of "hard" solders for germanium-containing silver alloys.

CLAIMS

1. A silver solder or brazing alloy of the Ag-Cu-Zn family containing more than 70 wt % Ag and from 0.5 to 3 wt% Ge.

2. The alloy of claim 1, containing 1.0-2.5 wt % Ge.

3. The alloy of claim 1, containing about 1.5 wt % Ge.

4. The alloy of any preceding claim, further comprising 1-3 wt % Sn.

5. The alloy of claim 4, comprising about 1 wt % Sn.

6. The alloy of any preceding claim containing 3 – less than 8 wt% Zn

7. The alloy of any preceding claim containing 4 - 5 wt% Zn

8. The alloy of any preceding claim, further comprising 0.05-0.4 wt % Si.

9. The alloy of claim 8, comprising about 0.1 wt% Si.

10. The alloy of any preceding claim, containing about 75 wt% Ag, about 18 wt% Cu and about 4.5 wt% Zn, about 1.5 wt% Ge and about 1 wt% Sn.

11. Use of the alloy of any preceding claim to solder or braze a joint in silver.

12. Use of the alloy of any of claims 1-10 to solder or braze a joint in Sterling silver.

13. Use of the alloy of any of claims 1-10 to solder or braze a joint in silver alloy of silver content at least Ag 92.5 wt% and containing germanium in an amount effective to impart firestain and/or tarnish resistance.

14. An alloy according to any of claims 1-10, which is in the form of rod, strip or wire.

15. An alloy according to any of claims 1-0, which is in the form of paste.

ABSTRACT

SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE

The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. They alloys are silver solder or brazing alloy of the Ag-Cu-Zn family containing more than 70 wt % Ag and from 0.5 to 3 wt% Ge. They can exhibit an advantageous combination of colour, flowability and firestain or tarnish resistance.